

# Ion Exchange and Submerged Soil

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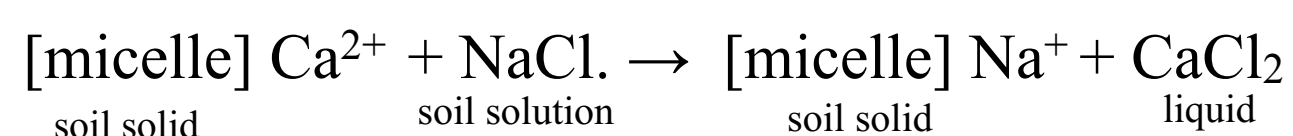
## Ion-exchange

It may be defined as the reversible process by which cations and anions are exchanged between solid and liquid phases or between solid phase, if in close contact with each other.

## Kinds of Ion-exchange

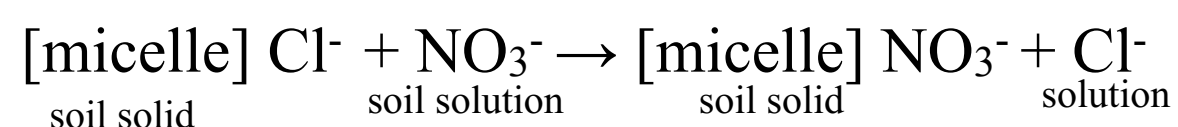
**Cation exchange :** It is the inter-change between a cation in solution and another on the surface of negatively charged clay or humus. Cation exchange reaction in soils mainly occur near the surface of clay and humus particles, called micelles. Each micelles may have thousands of negative charges that are neutralized by adsorbed or exchangeable cations. **OR** "Exchange of one positive ion by another is called cation exchange".

*Example-* If we want to replace  $\text{Ca}^{2+}$  from the micelle then the soil is leached with NaCl solution. The reaction is shown below-



The most important cation in soils are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Al}^{3+}$ .

**Anion exchange:** The basic principles of cation exchange also apply to anion exchange, except that the charges on the colloids are positive and the exchange is among negatively charged anions. A simple *example* of an anion exchange reaction below-



In general the relative order of anion exchange is  $\text{OH}^- > \text{H}_2\text{PO}_4^- > \text{SO}_4^{2-} > \text{NO}_3^-$ .

## Origin of Ion-exchange

Ion-exchange property of soil is intimately associated with the colloidal material of that soil. Soil colloids is the most reactive part of soil. Clay and humus particles exhibit colloidal properties. Clay is called inorganic colloid while humus is organic colloid. So colloids can bind both cations and anions. However, colloidal soil particles are mostly negatively charged and they hold cations only.

## Cation Exchange Capacity (CEC)

The CEC of soil is defined as, the sum of positive (+) charges of the adsorbed cation that a soil can adsorb at a specific  $\text{pH}$  (generally  $\text{pH}_7$ ). **OR** "CEC is the amount of exchangeable cations per unit weight of dry soil".

It is measured in milliequivalents of cations per 100 gm of soil and recently centimoles of positive charge/kg of soil [ $\text{cmol}(p^+)/\text{kg}^{-1}$ ].

It is one of the most important chemical properties of soils and is usually intimately related to soil fertility and plant nutrition. CEC of most soil increases with  $\text{pH}$ .

## Factors affecting CEC

The following factors affects the CEC-

- **Soil texture:** Fine textured (clay) soils tend to have higher CEC than sandy soils. CEC for clay soils usually exceeds 30 meq/100 gm while the value ranges from 0-5 for sandy soils.

- **Soil  $P^H$** : CEC of most soils increase with  $P^H$ . At very low  $P^H$  values, the CEC is very low.
- **Organic Matter content**: OM content of a soil affects the CEC. Higher OM content in a soil have higher CEC.
- **Amount of Kind of Clay**: Most morillonite has higher CEC in comparison to illite or kaolinite clay.

## Kinds of Soil Acidity

1. **Active acidity**: It may be defined as the acidity develops due to  $H^+$  and  $Al^{3+}$  ion concentration of the soil solution.
2. **Exchange acidity**: It may be defined as the acidity develops due to adsorbed by  $H^+$  and  $Al^{3+}$  ion on the soil colloids.

## Definition of BSP and Milliequivalent

**Base Saturation Percentage (BSP)**: The percentage of the total cation exchange capacity (CEC) saturated with basic cations is called Base Saturation Percentage (BSP). It is defined as the extent to, which the exchange complex of a soil is saturated with exchangeable cations, excluding  $H^+$  and  $Al^{3+}$ .

$$BSP = (S \div T) \times 100$$

Here,  $S$  = Basic cations in meq/100 gm soil.

$T$  = Total exchange capacity in milliequivalent per 100 gm soil.

**Milliequivalent**: The term milliequivalent may be defined as one milligram of Hydrogen or the amount of any other ion that will combine with or displace this amount of hydrogen.

$$1 \text{ meq } H^+ = 1 \text{ meq } Na^+ = 1 \text{ meq } K^+ = 1 \text{ meq } Ca^{++}$$

$$\text{OR, } 1 \text{ mg } H^+ = 23 \text{ mg } Na^+ = 39 \text{ mg } K^+ = 20 \text{ mg } Ca^{++}$$

## Importance of CEC in Soil/Agriculture

Cation exchange is an important reaction in soil fertility, in causing a correcting soil acidity and basicity, in changes or alternating soil physical properties and as a mechanism in purifying or altering percolating waters.

It is very important in soils because of the following relationships-

1. The exchangeable K is a major source of plant K.
2. The exchangeable Mg is often a major source of plant Mg.
3. The amount of lime, required to raise the  $P^H$  of an acidic soil, is greater as the CEC is greater.
4. Cation exchange sites hold  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$  and  $NH_4^+$  ions and slow losses by leaching.

## Causes of Negative charge Developed in Soil Colliods/Clay

2 Sources of Negative charges on clays-

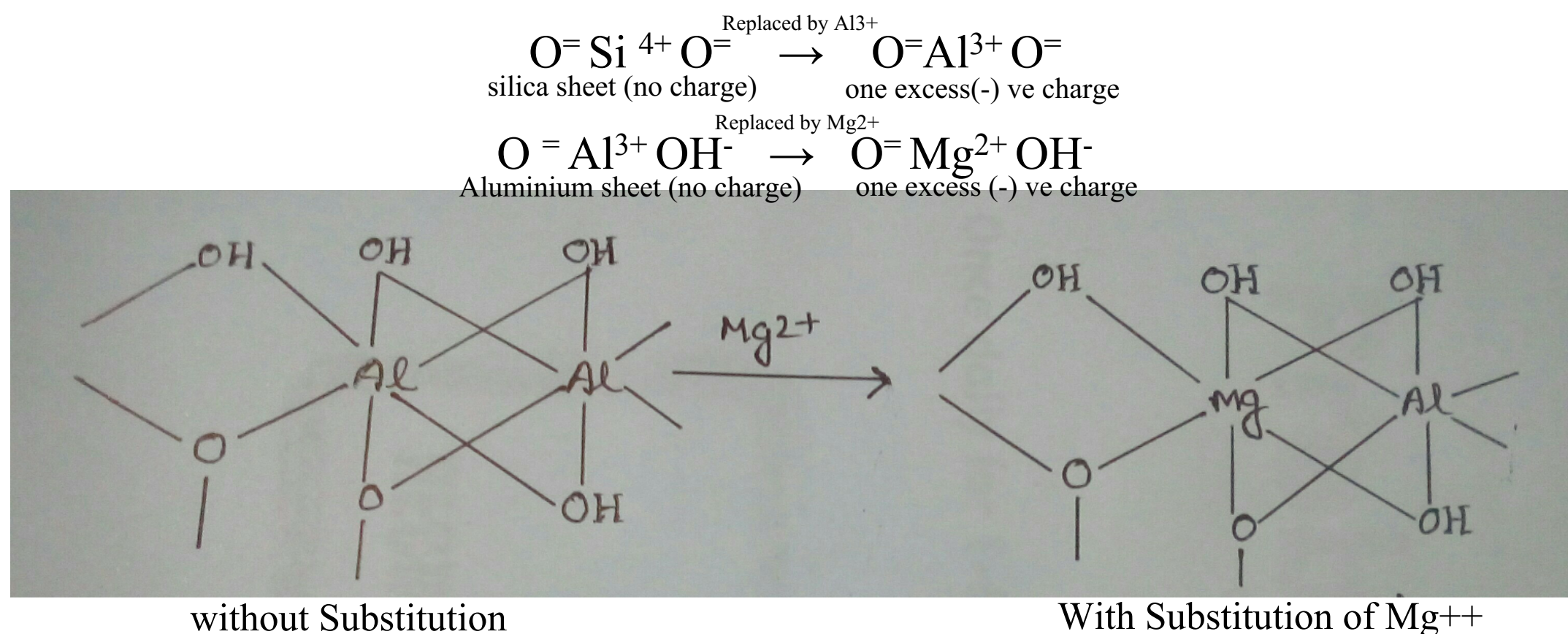


**1. Permanent negative charge-** Resulting from isomorphous substitution.

**2. P<sup>H</sup> depending charge-** Arising from ionization of functional group of solids/clays on the surface of soil solid.

**1. Permanent negative charge:** Permanent negative charge develops due to isomorphous substitution reaction. It is the substitution of one ion from another of similar size but lower positive valence within a crystal lattice.

This substitution occurs both tetrahedral and octahedral sheets. In silica sheet, Si<sup>4+</sup> replaced by Al<sup>3+</sup> and in Aluminium sheet, Al<sup>3+</sup> replaced by Mg<sup>2+</sup>/Fe<sup>2+</sup>.

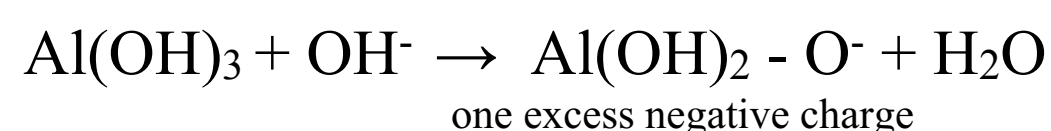


This is more common in 2:1 type clay mineral e.g. smectite, vermiculite and also in, 2:1 type of clay mineral (e.g. Chlorides) but less common in 1:1 type of clay minerals (e.g. kaolinite).

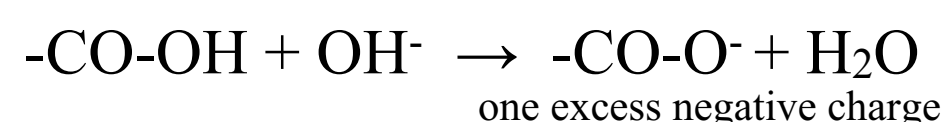
**2. P<sup>H</sup> depending charge-** This charge raising from the ionization of functional group attach to the organic structure. The total charges of soil particles in the sum of (-) ve and (+) ve charges and these total charges varies with p<sup>H</sup>. (+) ve charge is develop at high P<sup>H</sup>. Most soil have net (-) ve charge because of the (-) ve on layer silicates and organic matter but highly weathered soil dominated by all allopttane and iron and Aluminium oxides. e.g. Gibbsite- Al(OH)<sub>3</sub>.

The primary sources of P<sup>H</sup> dependent charge is considered is gain or loss of H<sup>+</sup> from functional groups on the surface of solids.

i) -OH group attach with inorganic structure. (e.g. clay minerals, sesqui oxides).



ii) -COOH, -C<sub>6</sub>H<sub>4</sub>OH, -NH<sub>2</sub> attached with organic structure (humus).



This (-) ve charge normally arises at P<sup>H</sup> = 7. This is more common in 1:1 type of clay minerals and less in 2:1 type clay minerals. Generally, 50% of the (-) ve charge develop on the 1:1 type of clay mineral is P<sup>H</sup> dependent. Where as, 5-10% charge on 2:1 type clay mineral is P<sup>H</sup> dependent.

## Buffering Capacity of Soil

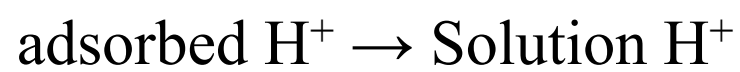
Buffering capacity of soil may be defined as the ability of a soil to resist the changes of P<sup>H</sup> due to the external chemical forces.

## Example of Buffering system-

### 1. *Weak acid + Strong base*



### 2. *Strong acid + weak base*



In soil adsorbed  $\text{H}^+$  (potential acidity) and solution  $\text{H}^+$  (active acidity) remain in equilibrium condition. When solution  $\text{H}^+$  is disturbed by lime e.g  $\text{Ca}(\text{OH})_2$  or  $(\text{NH}_4)_2\text{SO}_4$ . Then the adsorbed  $\text{H}^+$  is also disturbed to check  $\text{P}^{\text{H}}$  changes.

## Factors Affecting Buffering Capacity of Soil

It depends on 2 factors-

1. **Cation Exchange Capacity (CEC):** CEC depend on organic matter and clay content. When OM and clay content is high then CEC is high. Buffering capacity then rises with the increasing of CEC.
2. **Base Saturation Percentage (BSP):** Buffering capacity maximum when BSP is 50%.

$$\text{BSP} = (\text{\pounds Basic cation} / \text{Total cations}) \times 100$$

$$= (\text{The exchangeable bases} \times 100) / \text{CEC}.$$

### *Total cations-*

- Basic cations-  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ .
- Acid cations-  $\text{H}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{4+}$ .
- Neutral cations-  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ .

## Submerged Soil

The submerged soil are those soil, which remain under water for a considerable period of year.

### Causes of Submerged Soil

- High water table (ground water table).
- More rainfall.
- Formation of impervious layer in sub-surface soil.
- Formation of hard plough pan in soil.
- Impermeability of clay soil.

### Characteristics of Submerged Soil

1. The exchange between soil air and atmosphere is curtailed. The soil becomes devoid of molecular oxygen ( $\text{O}_2$ ).

2. The aerobic organism will ultimately die. But anaerobic will survive using combined oxygen ( NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>).

3. The Oxidized constituents of soil are reduced and the reduction occurs in a sequential manners follows-



4. The P<sup>H</sup> of acid soil increases and that of alkaline soil decreases and approaches neutrality.
5. The redox potential (E<sub>h</sub>) decreases.
6. The specific conductence increases.
7. Elements like Ca, Mg, Na, K, Zn, Cu, B do not undergo reduction. Their availability in soil may be hampered due to P<sup>H</sup> change.
8. Electrical conductivity increases.
9. Redox potential (E<sub>h</sub>) decrease during the first days and reaches minimum and then increases.
10. Water content is high and air content is very low or zero.
11. Gas exchange between soil and air/atmosphere is extremely limited.
12. Diffusion of gas nutrient is slow in water logged soil.
13. Leaching and gaseous loss of nutrient are high.
14. As the aerobic organism is died. So, decrease microbial activity and decrease OM status due to low decomposition.

Distinguish between Submerged and aerated Soil

Submerged Soil	Aerated Soil
Water content is higher than aerated soil, but air content is low.	Water content is relatively low but air content is high.
Gas exchange between soil and air is extremely limited.	Gas exchange between soil and air is high in above soil surface.
Microbial activity is low hence OM status also decrease.	Microbial activity is high.
Diffusion of gas and nutrient is slow in water logged soil.	Diffusion of gas and nutrient is higher than water logged soil.
Decomposition of OM is slow than aerated soil.	Decomposition of OM is higher than submerged soil.
Leaching and gaseous loss of nutrient is high.	Movement and loss of nutrient are limited.
Increase P <sup>H</sup> in acid soil and decrease P <sup>H</sup> in alkaline soil.	Salinity increases.
There is an oxidized layer on soil surface at the soil water inter-phase.	Oxidized layer extent to the ground water level.

Soil becomes reduced and reduced soil contains form of nutrient such as $\text{Fe}^{2+}$ , $\text{Mn}^{2+}$ , $\text{S}^{2-}$ , $\text{CH}_4$ , $\text{H}_2\text{S}$ etc.	Oxidation takes place and oxidation forms of nutrients such as $\text{NO}_3^-$ , $\text{Fe}^{3+}$ , $\text{SO}_4^{2-}$ etc.
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## Redox Potential

Redox potential means oxidation reduction potential. It is expressed as  $E_h$ . It is a single measure by which one can differentiate between oxidized and reduced condition of soil. Redox potential is measured by using platinum electrode. This is measured in terms of voltage. According to the voltage values, the soil can be grouped into 4 classes-

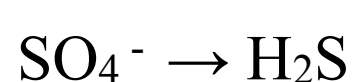
Class	$E_h$ (mv), $P^H = 7$ and temperature $25^\circ \text{C}$
Oxidized soil	+400 to +700 mv
Moderately reduced soil	+200 to +400 mv
Strongly reduced soil	-100 to +200 mv
Very strongly reduced soil	-300 to -100 mv

## Factors affecting Redox potential

1. With the decrease of  $\text{O}_2$ ,  $E_h$  value reduces rapidly.
2. As the  $E_h$  decreases,  $\text{CO}_2$  concentration increases and may reach upto toxicity level.
3. Under submerged condition of soil,  $E_h$  decreases during the first one day and reaches minimum.
4. The course rate and magnitude of  $E_h$  decreases depend on kind and amount of OM, the nature and content in electron acceptors and duration of submerged time.
5. The rapid initial decrease of  $E_h$  due to release of reducing substances accompanying oxygen depletion.
6. Temperature above and below  $25^\circ \text{C}$  retard the decrease in  $E_h$  but vary with soil. The effect is pronounced in acid soil but hardly noticeable in neutral soil and high in OM.
7. Aerated soil has  $E_h$  varying from +400 to +700 mv but in water logged soil, it varies from +230 to -300 mv.
8. If temperature, OM, concentration of solution, micro organism are increased then redox potential also increased.

## Transformation of S in submerged soil

(i) Reduction of sulphates to sulphides.



(ii) Reduction of S-containing amino acids, i.e. cystine, cysteine, methionine to  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and fatty acids.

(iii) Formation of sulphide with  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Cu}^{2+}$ .



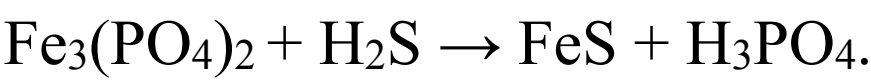


Transformation of P in submerged soil

(i) Formation of phosphites, hypophosphites and phosphine.

(ii) Increase of P-availability, due to-

- Reduction of Fe and Al phosphates
- Release of P from Fe-phosphate due to reduction with H<sub>2</sub>S.



- Change of soil P<sup>H</sup>.

Sequential reduction reaction in Submerged soil

System		E <sub>h</sub> (mv), P <sup>H</sup> = 7 at 25 <sup>o</sup> C
i) O <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup>	→	2H <sub>2</sub> O.....+820
ii) 2NO <sub>3</sub> <sup>-</sup> + 12H <sup>+</sup> +10e <sup>-</sup>	→	N <sub>2</sub> + 6H <sub>2</sub> O.....+740
iii) MnO <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup>	→	Mn <sup>2+</sup> + 2H <sub>2</sub> O.....+410
iv) Fe(OH) <sub>3</sub> + 3H <sub>2</sub> O + 1e <sup>-</sup>	→	Fe <sup>2+</sup> + 3H <sub>2</sub> O.....-180
v) SO <sub>4</sub> <sup>2-</sup> + 10H <sup>+</sup> + 8e <sup>-</sup>	→	H <sub>2</sub> S + 4H <sub>2</sub> O.....-210
vi) CO <sub>2</sub> + 8H <sup>+</sup> + 8e <sup>-</sup>	→	CH <sub>4</sub> + 2H <sub>2</sub> O.....-240
vii) N <sub>2</sub> + 8H <sup>+</sup> + 6e <sup>-</sup>	→	2NH <sub>4</sub> <sup>+</sup> .....-280
viii) 2H <sup>+</sup> + 2e <sup>-</sup>	→	H <sub>2</sub> .....-410
ix) H <sub>3</sub> PO <sub>4</sub> + 2H <sup>+</sup> + 2e <sup>-</sup>	→	H <sub>3</sub> PO <sub>3</sub> + H <sub>2</sub> O.....-700
x) H <sub>3</sub> PO <sub>3</sub> + 2H <sup>+</sup> + 2e <sup>-</sup>	→	H <sub>3</sub> PO <sub>2</sub> + H <sub>2</sub> O.....-920
xi) H <sub>3</sub> PO <sub>2</sub> + H <sup>+</sup> + e <sup>-</sup>	→	P + 2H <sub>2</sub> O.....-930

As the appearance of O<sub>2</sub> in the submerged soils, some oxidized soil compounds that can undergoes reduction is sequentially as the above system. The need for electron acceptors by anaerobic micro-organisms result in the reduction.

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